

METHOD OF PRODUCING THIN FILMS OF COMPOUND I-III-VI,
PROMOTING THE INCORPORATION OF III ELEMENTS IN THE FILM

The present invention relates to the production of
5 semiconductors of the I-III-VI₂ type in thin film form,
especially for the design of solar cells.

I-III-VI₂ compounds of the CuIn_(1-x)Ga_xSe_yS_(2-y) type
(where x is substantially between 0 and 1 and y is
10 substantially between 0 and 2) are regarded as very
promising and could constitute the next generation of
thin-film photovoltaic cells. These compounds have a
wide direct bandgap of between 1.05 and 1.6 eV, which
allows solar radiation in the visible to be strongly
15 absorbed.

Record photovoltaic conversion efficiencies have been
achieved by preparing thin films by evaporation on
small areas. However, evaporation is difficult to adapt
20 to the industrial scale because of problems of
nonuniformity and low utilization of raw materials.
Sputtering is better suited to large areas, but it
requires very expensive vacuum equipment and precursor
targets.

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There is therefore a real need for alternative, low-
cost atmospheric-pressure, techniques. The technique of
thin-film deposition by electrochemistry, in particular
by electrolysis, appears to be a very attractive
30 alternative. The advantages of this deposition
technique are numerous, and in particular the
following:

- deposition at ambient temperature and ambient
pressure in an electrolysis bath;
- 35 - possibility of handling large areas with high
uniformity;
- ease of implementation;
- low installation and raw material costs (no

special forming operation, high level of material utilization); and

- great variety of possible deposit shapes due to the localized nature of the deposit on the substrate.

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Despite extensive research in this field, the difficulties encountered relate to how to control the quality of the electrodeposited precursors (composition and morphology) and, more particularly, the difficulty
10 of inserting metals such as gallium or aluminum (elements III) whose electrodeposition potential is very cathodic.

I-III-VI₂ compounds in which:

- 15 - the element I corresponds to Cu;
 - the element III corresponds to In and to Ga and/or Al; and
 - the element VI corresponds to Se and/or S,
- will be denoted hereafter by the abbreviation CIGS.

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Moreover, the term "film" is understood to mean a thin layer deposited on a substrate, and the term "precursor film" is understood to mean a thin layer of overall composition close to I-III-VI₂ and obtained directly
25 after deposition by electrolysis, with no optional subsequent treatment.

As regards pure electrodeposition of CIGS (with no evaporation step), the morphology and the composition
30 of the precursors are very difficult to control, as the following documents indicate:

- "One step electrodeposited $\text{CuIn}_{1-x}\text{Ga}_x\text{Se}_2$ thin films: structure and morphology", M. Fahourme, F. Chraibi, M. Aggour, J.L. Delplancke, A. Ennaoui and
35 M. Lux-Steiner, 17th European Photovoltaic Solar Energy Conference, October 22 - 26, 2001, Munich, Germany; and
- " $\text{CuIn}_{1-x}\text{Ga}_x\text{Se}_2$ -based photovoltaic cells from electrodeposited precursor films", Materials Research Society Symposium - Proceedings, Volume 668, 2001,

pages H8101 - H8106, by R. N. Bhattacharya and Arturo M. Fernandes.

The most recent developments have involved an
5 evaporation step after the electrodeposition, so as to
increase the In and Ga contents of the electrodeposited
films. In these developments, especially those
described in document WO 01/78154, the
electrodeposition is an actual codeposition of the
10 elements Cu, In, Ga and Se (in order to obtain a
quaternary alloy) and employs a method of deposition in
a pH buffered electrolytic bath. The buffer solution is
composed of sulfamic acid and potassium biphthalate,
forming a buffer of the pHydrion (registered trademark)
15 type. Electrodeposited films that have given
photovoltaic cells using the hybrid method involving an
electrodeposition step followed by an evaporation step
have a dendritic morphology of low density.

20 The present invention aims to improve the situation.

For this purpose, it proposes a method of producing a
I-III-VI_y compound in thin film form, in which y is
close to 2, by electrochemistry, comprising the
25 following steps:

- an electrolysis bath comprising at least one
element III dissolved in the bath and at least two
electrodes immersed in the bath is provided, and
- a potential difference is applied between the
30 two electrodes in order to initiate the formation of a
thin film of I-III-VI_y on the surface of one of the
electrodes.

According to the invention, the electrolysis bath
35 furthermore includes at least one surfactant compound
in order to promote the incorporation of the element
III into said film.

Advantageously, the element III comprises gallium

and/or aluminum.

Preferably, the surfactant compound has a chemical formula $\text{CH}_3(\text{CH}_2)_n\text{O}-\text{SO}_3-\text{X}$, where n is greater than or
5 equal to 5 and X is an atomic species such as H , Na , Li or K .

In a preferred embodiment, the surfactant compound comprises sodium dodecylsulfate.

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Alternatively or additionally, the surfactant compound comprises 2-butyne-1,4-diol and/or maleic acid and/or succinic acid and/or fumaric acid and/or crotonic acid.

15 Preferably, the concentration of the surfactant in the electrolysis bath is substantially of the same order of magnitude as the concentration of gallium and/or aluminum.

20 Other advantages and features of the invention will become apparent on reading the detailed description below of embodiments given by way of nonlimiting examples, and from examining the drawings which accompany it, in which:

25 - figure 1 shows schematically a thin film obtained by implementing the method according to the invention;

- figure 2 shows schematically an electrolysis bath for implementing the method according to the
30 invention;

- figure 3 shows schematically the appearance of a thin film of the prior art, seen from above; and

- figure 4 shows schematically a sectional view of a thin film of the prior art, being formed.

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Referring to figure 1, copper diselenide and indium-gallium (as element III) layers CO are obtained at ambient pressure and ambient temperature by the electrodeposition of a thin precursor film of suitable

composition and morphology on a glass substrate S coated with molybdenum Mo.

5 The electrodeposition is carried out using an acid bath B (figure 2), stirred by blades M, containing an indium salt, a gallium salt, a copper salt and selenium oxide in solution. The concentrations of these precursor elements are between 10^{-4} and 10^{-2} M, where the symbol "M" corresponds to the unit "mole per liter". The pH of
10 the solution is fixed between 1 and 4.

Three electrodes An, Ca and REF, including:

- a molybdenum electrode Ca on which the thin film is formed by electrodeposition; and
- 15 - a mercurous sulfate reference electrode REF,
are immersed in the bath B.

The electrical potential difference applied to the molybdenum electrode is between -0.8 and -1.4 V
20 relative to the reference electrode REF.

Films with a thickness of between 1 and 4 microns are obtained with current densities of between 0.5 and 10 mA/cm².

25 Under defined composition, solution stirring and potential difference conditions, it is possible to obtain dense adherent films of homogeneous morphology, the composition of which is close to the stoichiometric composition: Cu (25%); In+Ga (25 + ϵ %) and Se (50%),
30 with an (In+Ga)/Cu atomic ratio slightly greater than 1. It is thus possible to form deposits on areas of 10 x 10 cm².

35 However, the incorporation of gallium in order to form thin CGIS films often poses a problem, both from the standpoint of their morphology and their composition. Referring to figure 3, the precursor layers CO, being formed by electrolysis under conventional conditions,

exhibit protuberances PR on the surface, these making a nonzero angle α relative to the principal plane of the surface of the layer (figure 4). Such a morphology of the thin film, which is particularly rough on its surface, is not compatible with the manufacture of photovoltaic cells, which require interfaces that are as parallel and as plane as possible in order to limit light loss and above all to avoid local short circuits (or shunts).

Furthermore, the volume composition of these deposits is lean in gallium (generally less than 5%) and in any case less than that initially desired.

The approach proposed in document WO 01/78154 consists in controlling the acidity of the electrolysis bath in order to ensure that its pH is stable and, consequently, to promote incorporation of gallium (an element whose deposition potential is very negative) into the CIGS layers being formed. For this purpose, the above document provides a buffer solution comprising sulfamic acid and potassium biphthalate in concentrations that are sufficient to ensure stability of the pH. $\text{CuIn}_{(1-x)}\text{Ga}_x\text{Se}_2$ films are then obtained with x close to 9%.

In another approach, the present invention proposes to add one or more surfactant additives to the electrolysis bath in order to form the CIGS films. $\text{CuIn}_{(1-x)}\text{Ga}_x\text{Se}_2$ films obtained by implementing the method according to the invention have a satisfactory morphology and a percentage x of gallium close to, or even greater than the aforementioned 9% value, as will be seen later with reference to a preferred embodiment.

One possible explanation of this improvement in the quality of the films by adding surfactants to the bath is the following. The addition of a surfactant compound, acting in the bath by being adsorbed on the

electrode Ca on which the thin film forms, makes it possible to modify the surface tension at the interface between the thin film being formed and the solution of the bath. Thus, the activation energy for the reaction of incorporating the gallium combined with selenium into the thin film is lowered. The mixing of gallium with other elements, Cu, In and Se, therefore makes it possible to obtain a homogeneous morphology of the film, and a composition rich in gallium.

Another possible explanation, in addition to the above one, is that the surfactants used may furthermore play an inhibiting role in the hydrogen evolution reaction usually observed in electrolysis. This would allow more cathodic potentials to be applied, thus promoting the incorporation of gallium.

A leveling effect of the surfactants added may also be noted, allowing the surface of the film being formed to be made plane.

Thus, according to the invention, one or more surfactant additives, for improving the morphology and/or changing the relative ratios of the various electrodeposited elements (Cu-In-Ga-Se), are added to the solution. It will be understood that their main role is to help in the insertion of gallium into the precursor layers. The amount of gallium that can be inserted into the films may vary from 0 to 30% (in atomic percentage). The concentration of the additives may vary from 10^{-5} to 10^{-2} M.

Given below are various embodiments of the invention, with the following as surfactant additives:

- sodium dodecylsulfate;
- 2-butyne-1,4-diol;
- succinic acid;
- fumaric acid; and
- maleic acid.

Preferred embodiment "sodium dodecylsulfate"

A typical deposit was produced from an acid bath whose concentrations of the precursor elements and of the surfactant $\text{CH}_3(\text{CH}_2)_{11}\text{OSO}_3\text{Na}$ were the following:

$$[\text{CuSO}_4] = 4.5 \times 10^{-3} \text{ M};$$

$$[\text{In}_2(\text{SO}_4)_3] = 2.5 \times 10^{-3} \text{ M};$$

$$[\text{Ga}_2(\text{SO}_4)_3] = 2.5 \times 10^{-3} \text{ M};$$

$$[\text{H}_2\text{SeO}_3] = 7.5 \times 10^{-3} \text{ M};$$

$$[\text{CH}_3(\text{CH}_2)_{11}\text{OSO}_3\text{Na}] = 20 \times 10^{-3} \text{ M}$$

The precursors were deposited by a cathodic reaction for a fixed potential, namely -1.1 V relative to the electrode REF. The current density was -5 mA/cm².

Table I: Analysis of the composition of an electrodeposited CIGS film from a solution containing sodium dodecylsulfate.

Element	at%
Cu	20.70
Ga	10.27
Se	50.94
In	18.10

Advantageously, the morphology of the film was very homogeneous.

More generally, it may be indicated that the addition of surfactants of formula $\text{CH}_3(\text{CH}_2)_n\text{O-SO}_3\text{-X}$ (where n is greater than or equal to 5 and X is an atomic species such as H, Na, Li or K) gave satisfactory results.

Second embodiment: "2-butyne-1,4-diol"

A typical deposit was produced from an acid bath whose concentrations of precursor elements and of the surfactant $\text{HO-CH}_2\text{-C}\equiv\text{C-CH}_2\text{-OH}$ were the following:

$$[\text{CuSO}_4] = 4.5 \times 10^{-3} \text{ M};$$

$$[\text{In}_2(\text{SO}_4)_3] = 2.5 \times 10^{-3} \text{ M};$$

$$[\text{Ga}_2(\text{SO}_4)_3] = 2.5 \times 10^{-3} \text{ M};$$

$$[\text{H}_2\text{SeO}_3] = 7.5 \times 10^{-3} \text{ M};$$

$$[\text{HO}-\text{CH}_2-\text{C}\equiv\text{C}-\text{CH}_2-\text{OH}] = 20 \times 10^{-3} \text{ M}.$$

5 The precursors were deposited by a cathodic reaction with a potential set at -1.1 V relative to the electrode REF. The current density was -5 mA/cm².

10 Table II: analysis of the composition of a CIGS film electrodeposited from a solution containing 2-butyne-1,4-diol.

Element	at%
Cu	23.10
Ga	1.80
Se	53.50
In	21.54

15 The morphology of the film was not very homogeneous. However, no debonding of the film was observed.

Third embodiment of the invention "maleic acid"

20 A typical deposit was produced from an acid bath whose concentrations of precursor elements and of the surfactant HO₂C-CH=CH-CO₂H were the following:

$$[\text{CuSO}_4] = 4.5 \times 10^{-3} \text{ M},$$

$$[\text{In}_2(\text{SO}_4)_3] = 2.5 \times 10^{-3} \text{ M},$$

$$[\text{Ga}_2(\text{SO}_4)_3] = 2.5 \times 10^{-3} \text{ M},$$

$$[\text{H}_2\text{SeO}_3] = 7.5 \times 10^{-3} \text{ M},$$

25 $[\text{HO}_2\text{C}-\text{CH}=\text{CH}-\text{CO}_2\text{H}] = 20 \times 10^{-3} \text{ M}.$

The precursors were deposited by a cathodic reaction for a potential set at -1.1 V relative to the electrode REF. The current density was -5 mA/cm².

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Table III: analysis of the composition of a CIGS film electrodeposited from a solution containing maleic acid.

Element	at%
Cu	23.32
Ga	3.10
Se	53.32
In	20.26

The morphology of the film was substantially homogeneous.

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Fourth embodiment: "succinic acid"

A typical deposit was produced from an acid bath whose concentrations of precursor elements and of the surfactant $\text{HO}_2\text{-CH}_2\text{-CH}_2\text{-CO}_2\text{H}$ were the following:

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$$[\text{CuSO}_4] = 4.5 \times 10^{-3} \text{ M},$$

$$[\text{In}_2(\text{SO}_4)_3] = 2.5 \times 10^{-3} \text{ M},$$

$$[\text{Ga}_2(\text{SO}_4)_3] = 2.5 \times 10^{-3} \text{ M},$$

$$[\text{H}_2\text{SeO}_3] = 7.5 \times 10^{-3} \text{ M},$$

$$[\text{HO}_2\text{-CH}_2\text{-CH}_2\text{-CO}_2\text{H}] = 20 \times 10^{-3} \text{ M}.$$

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The precursors were deposited by a cathodic reaction for a potential set at -1.1 V relative to the electrode REF. The current density was -5 mA/cm².

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Table IV: analysis of the composition of a CIGS film electrodeposited from a solution containing succinic acid.

Element	at%
Cu	23.69
Ga	3.99
Se	53.33
In	19.99

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The morphology of the film was advantageously homogeneous.

Fifth embodiment: "fumaric acid"

A typical deposit was produced from an acid bath whose concentrations of precursor elements and of the surfactant $\text{HO}_2\text{-CH-CH-CO}_2\text{H}$ were the following:

- 5 $[\text{CuSO}_4] = 4.5 \times 10^{-3} \text{ M},$
 $[\text{In}_2(\text{SO}_4)_3] = 2.5 \times 10^{-3} \text{ M},$
 $[\text{Ga}_2(\text{SO}_4)_3] = 2.5 \times 10^{-3} \text{ M},$
 $[\text{H}_2\text{SeO}_3] = 7.5 \times 10^{-3} \text{ M},$
 $[\text{HO}_2\text{-CH-CH-CO}_2\text{H}] = 20 \times 10^{-3} \text{ M}.$

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The precursors were deposited by a cathodic reaction for a potential set at -1.1 V relative to the electrode REF. The current density was -5 mA/cm².

- 15 **Table V:** analysis of the composition of a CIGS film electrodeposited from a solution containing **fumaric acid**.

Element	at%
Cu	24.54
Ga	2.85
Se	52.60
In	20.00

- 20 The morphology of the film was substantially homogeneous.

More generally, the additive within the meaning of the invention may be a surfactant compound taken from the
25 following two classes:

- the surfactant compounds, the molecule of which contains the $\text{X-SO}_3\text{-Y}$ or $\text{Z-SO}_2\text{-Z'}$ group, in which:
 - o Y is an element taken from H, Na, Li, K;
 - o X is an unsaturated (ethylenic, aromatic or
30 acetylenic) group that may contain hetero atoms, with any number of carbon atoms, or else a saturated group that may contain hetero atoms;
 - o Z and Z' are saturated or unsaturated groups that may contain hetero atoms (S, N or the

like); and

- compounds whose molecule possesses at least one polar group: -OH- COOH, -S (or other hetero atom) and/or an unsaturated group: alkene, alkyne, aromatic (with or without a hetero atom), allowing the molecule to be adsorbed during electrodeposition.

Each compound of one of the two families may be used by itself or as a mixture. The same compound may belong to both families (if it possesses at least one unsaturated group and at least one SO₂ group).

It should be pointed out that these surfactant compounds differ from the usual organic solvents whose solvation role acts only on the solution of the bath. They also differ from the organic additives introduced into the electrolysis bath for stabilizing the pH.

The surfactant compounds described above may be easily used for any type of electrolysis bath for the electrodeposition of I-III-VI systems such as Cu-In-Ga-Al-Se-S.

The surfactants allowing gallium to be inserted into the precursor films thus make it possible to solve several difficulties described in the prior art (poor control of the morphology, of the composition of the precursors, in particular as regards the gallium content, and the difficulty of extending to large areas).

Of course, the present invention is not limited to the embodiment described above by way of example, rather it extends to other variants.

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Thus, it will be understood that aluminum, as element III, poses substantially the same problems of incorporation into the Cu-In-Al-Se films as gallium. In this regard, the invention applies also to the production of such

films. Moreover, indium is usually introduced in excess into the solution of the bath in order to promote its incorporation into the film, indium combining, as element III, with selenium. It may be pointed out that
5 the addition of surfactants to the bath ought also to promote the incorporation of indium as element III, into the film.

Moreover, it should also be pointed out that crotonic
10 acid, as surfactant additive, has also provided satisfactory results.